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N63-13442
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Technical Report No. 32-360

Structural Transformation in Pyrolytic Graphite Accompanying Deformation

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JET PROPULSION LABORATORY
CALIFORNIA INSTITUTE OF TECHNOLOGY
PASADENA, CALIFORNIA

November 1, 1962

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT NO. NAS 7-100

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ABSTRACT

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Electron microscopy and x-ray diffraction techniques have been used to follow the structural changes which accompany deformation in one lot of pyrolytic graphite when stress is applied parallel to the substrate direction. Basal slip and an increase in preferred orientation account for deformations up to 20%. Fracture across the basal planes with subsequent basal slip and an increase in porosity and a very slight increase in preferred orientation account for deformations above 20%. Rows of etch pits which may be dislocations parallel to the substrate direction were observed in a specimen heated without load to 3000°C.

I. INTRODUCTION

When pyrolytic graphite is heated above the deposition temperature it undergoes a transformation which results in an increase in preferred orientation, a decrease in turbostratic structure, permanent growth parallel to the basal planes, shrinkage perpendicular to the basal planes, and an elimination of the growth cone structure (Ref. 1 through 4). The degree of completeness of this transformation, or graphitization as it may be called, depends upon the temperature to which the material is heated. The temperature range for this transformation varies from lot to lot of pyrolytic graphite, but generally it is initiated after heating to 2600°C (Ref. 2) and is completed after heating to 3200°C (Ref. 5). If heating is accompanied by deformation in the basal plane direction, then the degree of completeness is greater at a given temperature, or the transformation can be initiated at a lower temperature.

One explanation given (Ref. 6) for the increase in tensile strength of pyrolytic graphite in the basal plane direction over the range from room temperature to 2760°C is based upon an increase in ductility and this strain-induced structural transformation. From room temperature to approximately 2200°C the increase could be due to an improvement in ductility which would relieve stress concentrations associated with low-angle grain boundaries within the growth cones and large-angle boundaries at the edges of growth cones (Ref. 7), or to a reduction of the "frozen-in-stresses" (Ref. 8) associated with the anisotropic thermal expansion of pyrolytic graphite. The increase in tensile strength above 2200°C could be due to a transformation or graphitization accompanying the deformation which increases with temperature.

This Report presents the structural transformation in one lot of pyrolytic graphite after heating to 3000°C and after various amounts of deformation at 2760°C. Transformation was followed by crystallographic and preferred-orientation measurements and by electron microscope examination of the basal plane surfaces and edges of the graphite.

II. TESTING EQUIPMENT AND PROCEDURE

The pyrolytic graphite[a] used in this study was deposited from CP methane at 2100°C on flat plates of synthetic graphite approximately 4 x 24 in. The gas flow rate was held at 5 l/min for 30 hr and then at 10 l/min for 30 hr. The gas pressure was maintained at 6.2 mm of Hg absolute. The final thickness was approximately 0.3 in., and the as-deposited density was 2.19 gm/cc. The as-deposited structure (Fig. 1) shows the material to be of medium grain size and primarily substrate nucleated with some regenerative nucleation.

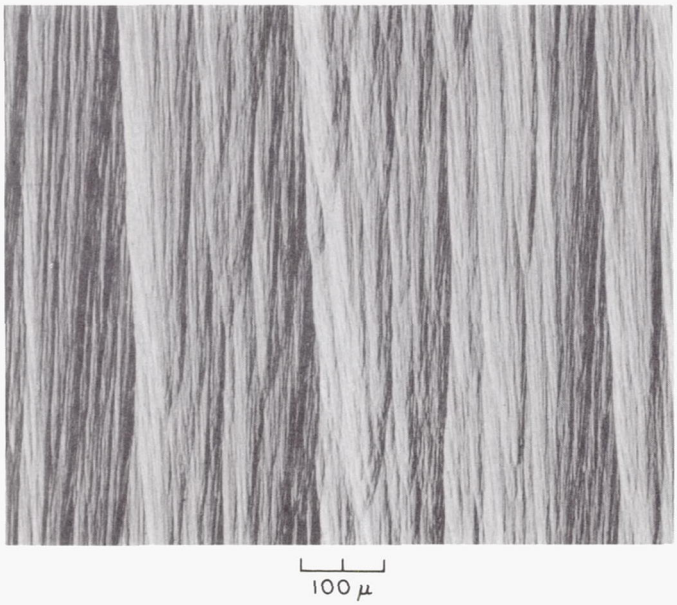


Fig. 1. Microstructure of edge of basal planes of as-deposited pyrolytic graphite lot 170

The test equipment used to strain the specimens at 2760°C has been described (Ref. 2 and 9), and the tensile properties of this lot 170 pyrolytic graphite have been previously reported (Ref. 6).

[a]Produced by High Temperature Material, Inc.

Unit cell and crystallite dimensions were calculated from x ray diffractometer data obtained from powdered samples using standard techniques (Ref. 10) with nickel-filtered copper radiation. Sodium chloride was used as an internal standard to correct for instrumental errors. Percent graphitization was calculated from the unit-cell height which was averaged from the (002) and (004) reflections and from curves of the combined data of Franklin (Ref. 11) and Bacon (Ref. 12).

Electron micrographs were prepared[b] by standard parlodian and vapor deposited carbon replica techniques and shadow casting with chromium (Ref. 13). Freshly cleaved surfaces were used for examination of the top of the basal planes. For examination of the edges of the basal planes the specimen was polished using standard metallographic techniques down to 0.1-micron alumina powder. This was followed by cathodic etching in an apparatus similar to that described by McCutcheon (Ref. 14), using argon as the ionized gas with an etching time of approximately 20 min.

Preferred orientation measurements were made on thin rod specimens approximately 0.02 in. square by ¼- to ½-in. long. These were cut from the gage section of the tensile specimens with the ¼- to ½-in. dimension parallel to the loading direction. The experimental procedure for making orientation measurements was similar to that described by others (Ref. 1, 3, and 15). Briefly this was as follows: The specimen was mounted on a single crystal goniometer which was affixed to a 360-deg. rotating stage. This assembly was mounted in place of the specimen holder post on a diffractometer. The specimen axis was aligned parallel to the height of the x ray beam and the diffractometer was set at the Bragg angle for the most intense (002) graphite reflection. The specimen was rotated and intensity of this reflection plotted as a function of angle of rotation.

[b]By Sloan Research Industries, Inc.

III. DISCUSSION OF RESULTS

Pyrolytic graphite may be described as polygonal zones or grains connected by tilt-boundaries, and could be represented by a stack of overlapping, wrinkled sheets (Ref. 3, 4, and 7) since the graphite basal planes are more or less parallel to the deposition surface. The electron micrograph of the top of the basal planes, (Fig. 2) shows such a wrinkled sheet structure for the as-deposited lot 170 pyrolytic graphite. Polygonal zones approximately 1000 Å in diameter are apparent. The electron micrograph of the edge of the basal planes (Fig. 2) shows a faint outline of the columnar growth cone structure. From x ray line broadening measurements, an average crystallite height of 240 Å and an average crystallite width of approximately 200 Å were calculated. The magnification used for Fig. 2 was not high enough to show individual crystallites of this size; however, zones of 3 to 5 times this size are visible in the upper micrograph of Fig. 2. Observation of zones approximately 300 to 1000 Å in diameter has been recently reported (Ref. 16).

After heating to 3000°C this lot of pyrolytic graphite showed an increase in density to 2.22 gm/cc, a permanent growth of 5% in the basal plane direction, and shrinkage of 11% perpendicular to the basal planes. Stover (Ref. 3) has made similar observations on other lots of pyrolytic graphite and has explained the growth phenomena as dewrinkling of the sheets due to thermally activated creep and basal slip resulting in elimination of the low-angle grain boundaries. That dewrinkling has occurred is clearly seen by comparing the electron micrograph of the top of the basal planes shown in Fig. 3 with that shown in Fig. 2. As seen in the lower micrograph (Fig. 3) the structure shows rows of etch pits which are parallel to the substrate direction. Some of these etch pits are 500 to 2000 Å in length and may be microcracks caused by separation between basal planes within an individual crystallite. Other etch pits may be dislocations. As has been found by Tsuzuku (Ref. 17), these dislocations may have been produced by stresses occurring within the structure during graphitization. Additional work will be necessary to provide a clear understanding of the origin of these etch pits. No evidence of etch pits in a non-basal plane direction, as has been reported (Ref. 18), was observed in the present work.

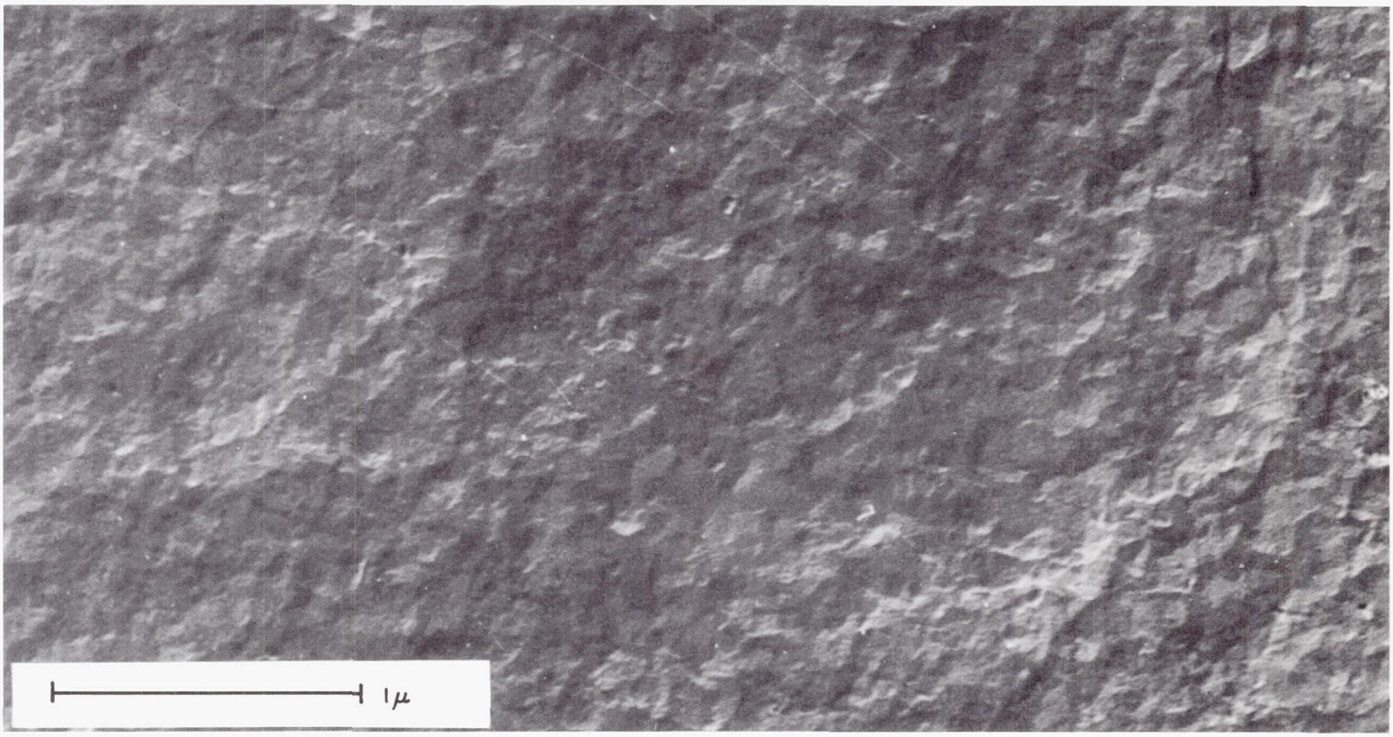
The large faint oval-shaped zones visible in the lower micrograph (Fig. 3) are from 1000 to 3000 Å in width and from 3000 to 6000 Å in height. Crystallites 1000 Å high were determined by x ray line broadening techniques after heating this lot of pyrolytic graphite to 3000°C. The visible oval-shaped zones are not markedly different in size from these crystallite dimensions.

Changes in the appearance of the surface and edges of the basal planes of this lot of pyrolytic graphite accompanying the transformation which occurs during deformation parallel to the basal plane direction can be seen in the electron micrographs of Fig. 4 and 5. As seen in Fig. 4, the amount of dewrinkling increases with increasing deformation. After 20% and 39% deformation the surface of the basal planes appears to be very smooth except for cleavage lines.

Electron micrographs of the edges of the basal planes after various amounts of deformation are shown in Fig. 5. These can be compared with the lower micrograph in Fig. 2 which is for the as-deposited material. The lines which are present in the micrographs of Fig. 5 are parallel to the basal plane direction, and have the general appearance of slip lines commonly seen in the structure of deformed metals. Differences in the detailed appearance of these lines may not be significant, since such differences could be due to differences in the etching procedure or could be due to the replicating technique. The data are too limited to identify the exact source of these lines. It is possible that they are rows of etch pits similar to those seen in the lower micrograph of Fig. 3, but which are unresolved in Fig. 5.

It is interesting to compare these changes in structure with changes in preferred orientation (Fig. 6) and crystallographic parameters (Table 1) which accompany deformation. The data in Table 1 show a marked increase in percent graphitization for deformations up to approximately 10% with only a slight increase for deformation between 10% and 39%. The crystallite height, L_c, which is also a measure of the crystal perfection, increases nearly uniformly with deformation up to 39%. Although the crystallite width, L_a, was not determined it would be expected to show a similar uniform increase. It is interesting to note that heating to 3000°C with no applied stress results in a higher degree of graphitization and a larger crystallite size than deforming 39% in the basal plane direction at 2760°C.

The data given in Fig. 6 show how preferred orientation changes with deformation at 2760°C. The misorientation angle shown in this figure was taken as one half the peak width at half maximum intensity of the (002)

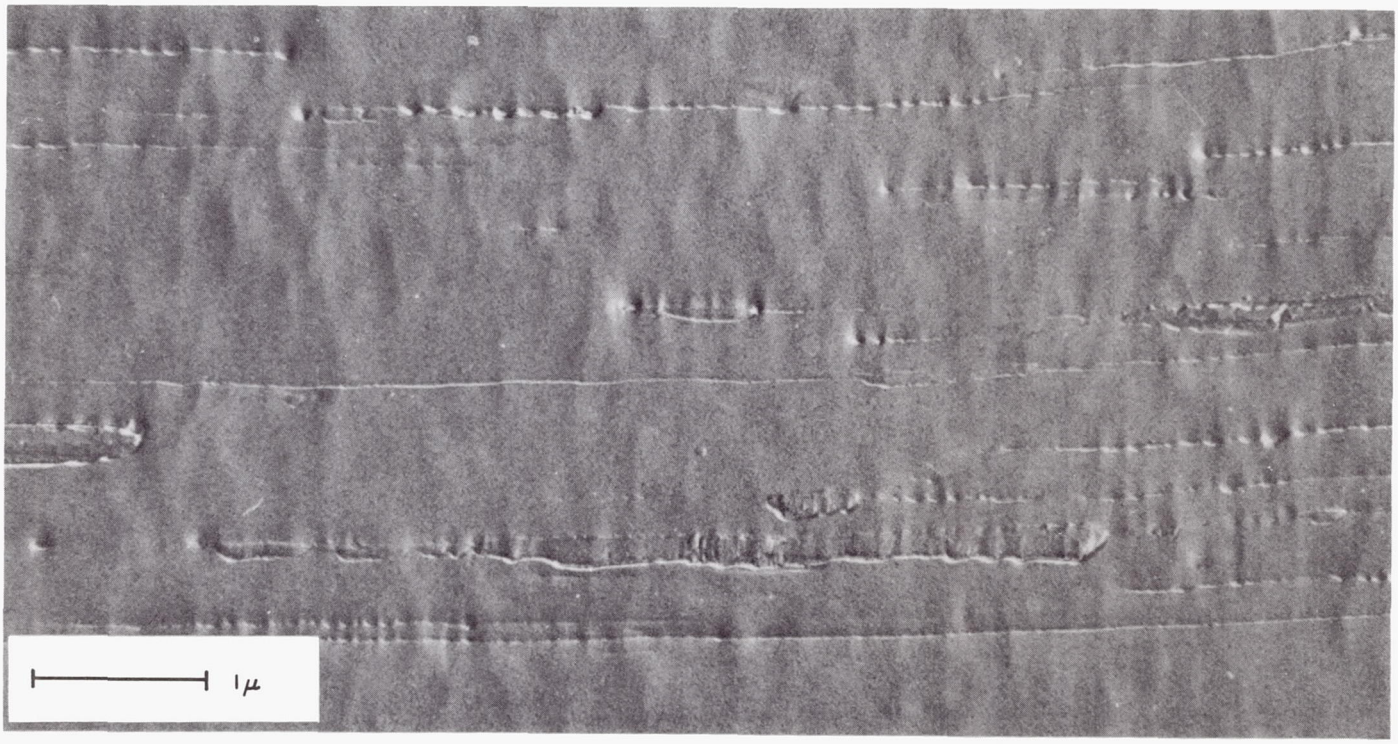


TOP OF BASAL PLANES

EDGE OF BASAL PLANES

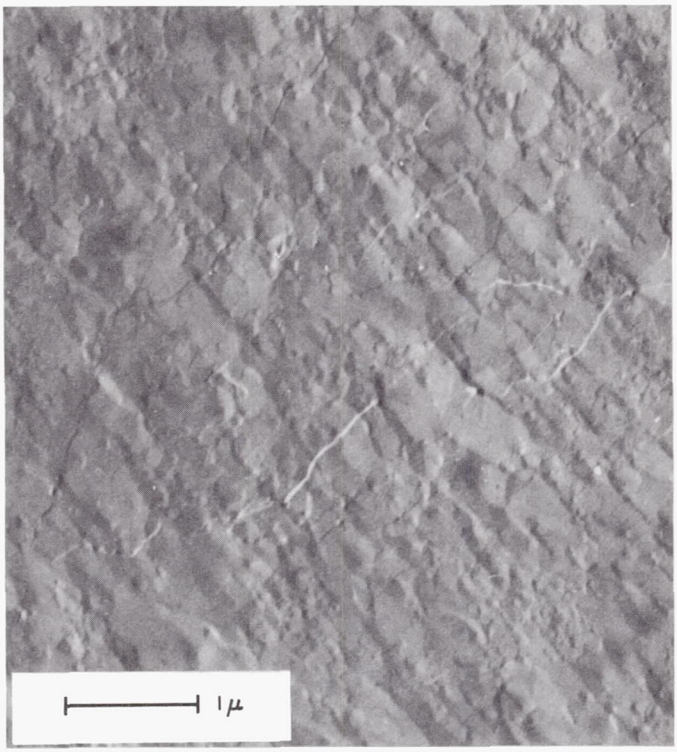
Fig. 2. Electron micrographs of as-deposited pyrolytic graphite lot 170

TOP OF BASAL PLANES



EDGE OF BASAL PLANES

Fig. 3. Electron micrographs of pyrolytic graphite after heating to 3000°C lot 170



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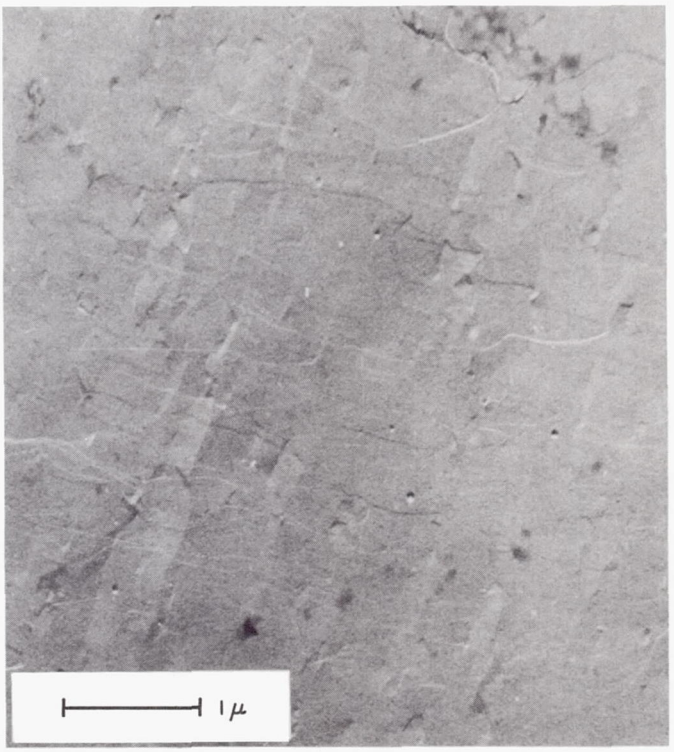

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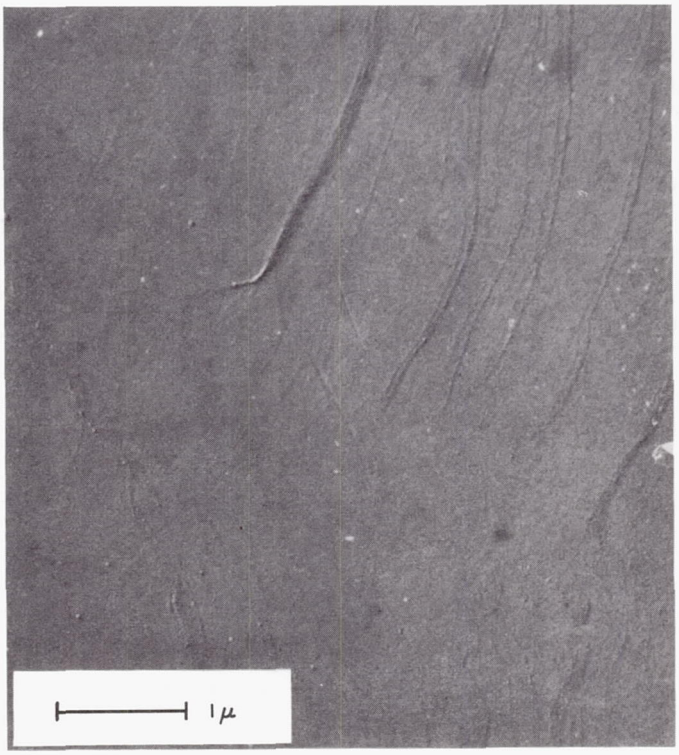

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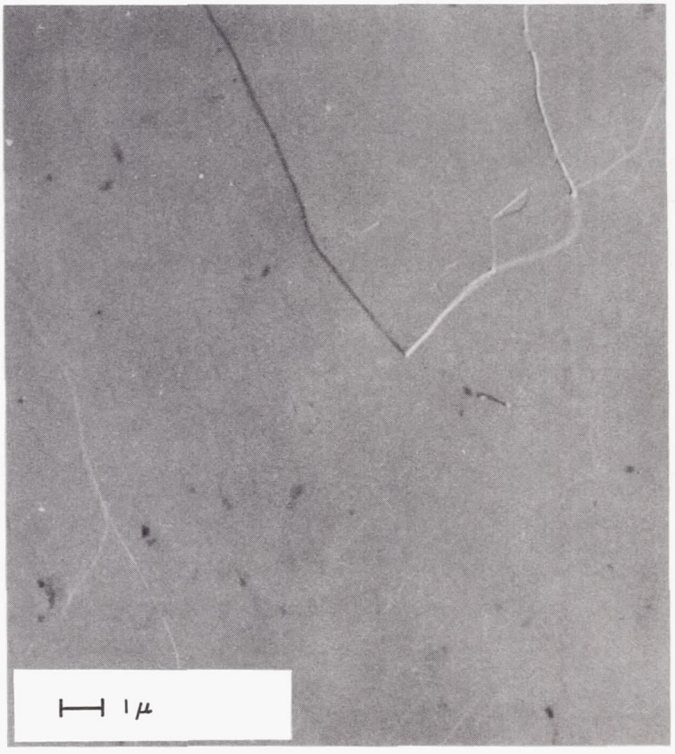
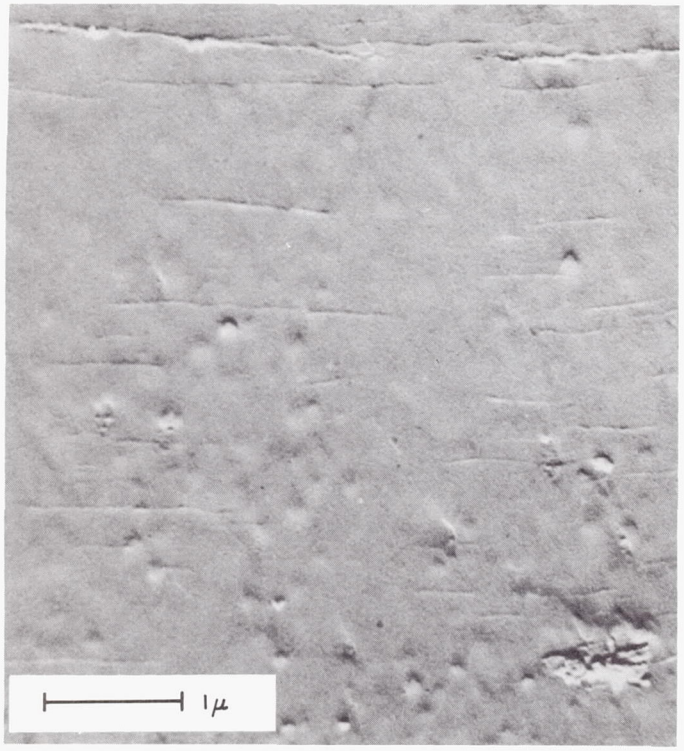


39%

Fig. 4. Electron micrographs of the basal plane surface of pyrolytic graphite after various amounts of deformation at 2760°C lot 170



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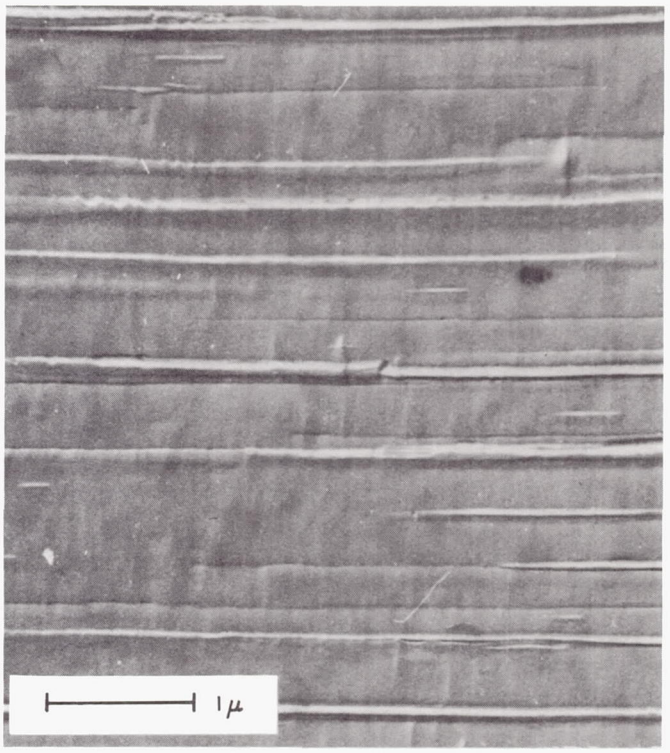

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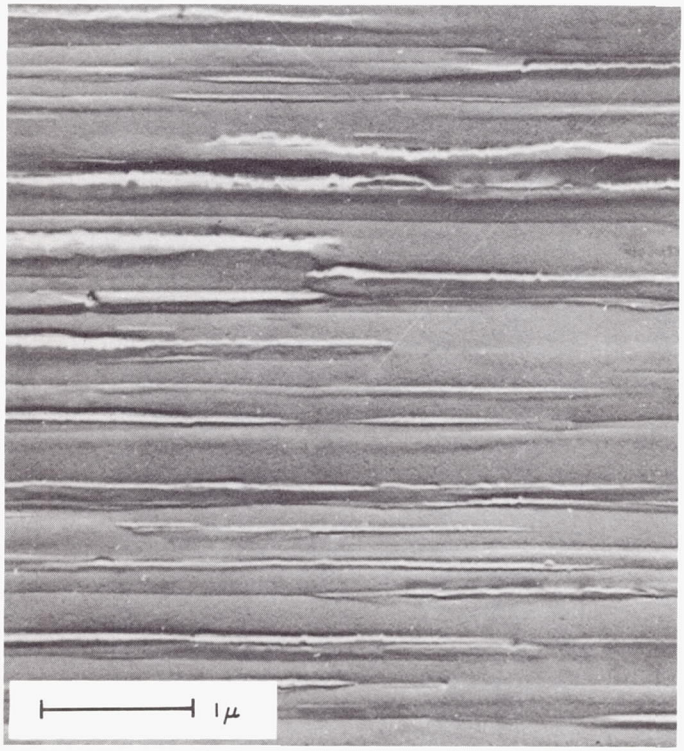

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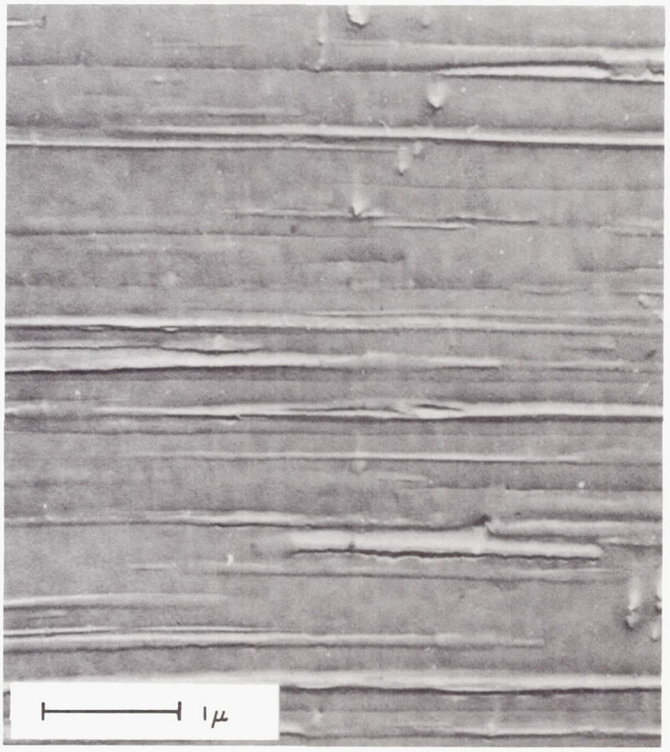


39%

Fig. 5. Electron micrographs of edge of basal planes of pyrolytic graphite after various amounts of deformation at 2760°C lot 170

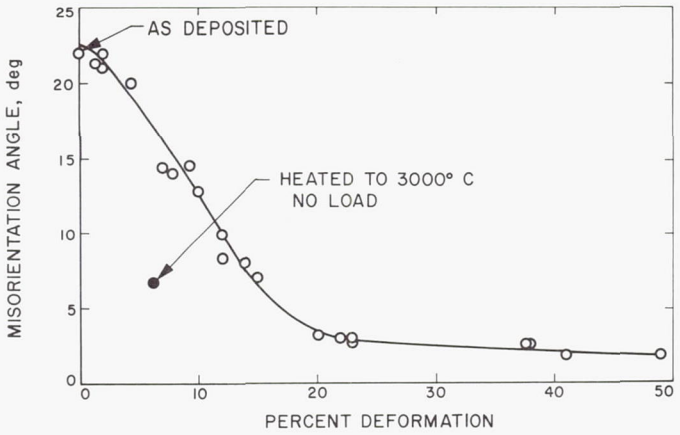


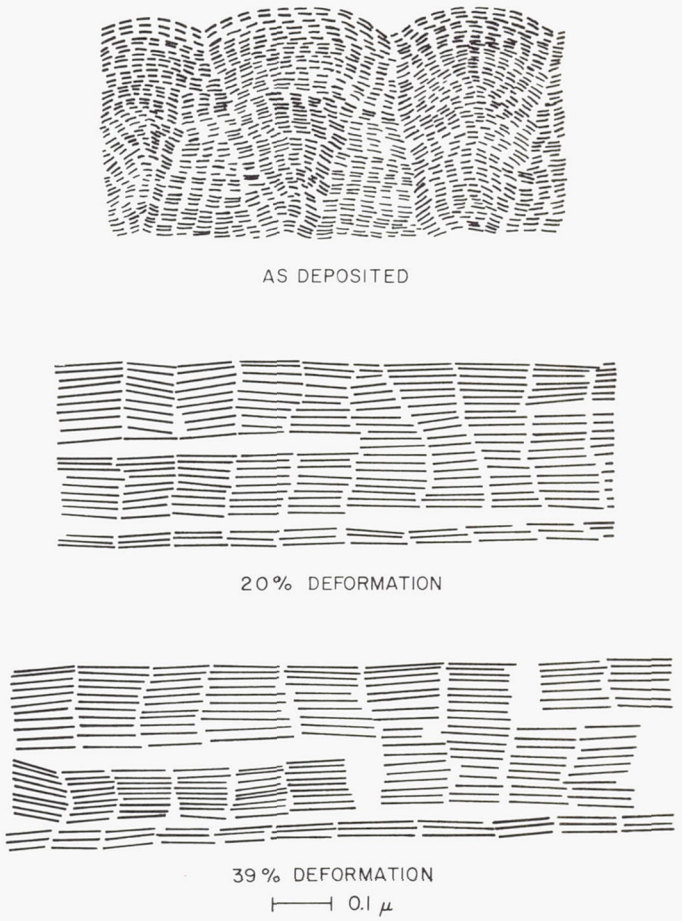
Fig. 6. Effect of heating to 3000°C and deforming at 2760°C on the preferred orientation of pyrolytic graphite lot 170

graphite peak from a plot of angle of specimen rotation vs normalized intensity. With the geometry and alignment procedure used this misorientation angle indicates the average angle which the basal planes make with the cleavage direction. Thus a decrease in the misorientation angle means an increase in preferred orientation. It should be noted that the preferred orientation increases uniformly with increasing deformation up to approximately 20%. After deformations greater than 20% there is very little change in preferred orientation probably because the material is almost perfectly oriented.

Also shown on Fig. 6 is the preferred orientation for a specimen heated to 3000°C with no applied stress. Although this treatment resulted in a higher degree of graphitization and a larger crystallite size than deforming 39% (Table 1), the preferred orientation (Fig. 6) is greater after either 20% or 39% deformation.

Table 1. Crystallographic parameters of pyrolytic graphite lot 170

Deformation at 2760°C, %	Unit cell height, C_o, Å	Percent Graphite	Crystallite Dimensions	
			Height, L_c, Å	Width, L_a, Å
as deposited	6.84	12	240	200
6	6.757	47	390	—
10	6.731	68	721	—
20	6.728	71	930	—
39	6.725	75	1600	—
heated to 3000°C	6.717	84	2100	1000



7. Deformation model of pyrolytic graphite.

Considering all of these data it would appear that the deformation of pyrolytic graphite produced by stressing in a direction parallel to the substrate can occur by several different mechanisms which may be described by the two dimensional model shown in Fig. 7. The as-deposited pyrolytic graphite structure is thought to be similar to the "anthracitic structure" described by Hirsch (Ref. 19) and the "graphitizing carbon structure" described by Franklin (Ref. 20); however, the pyrolytic graphite has no porosity and has a higher degree of preferred orientation.

Deformations up to approximately 20% occur by basal plane slip and basal plane orientation. The fact that the basal planes are initially at some angle with respect to the stress direction and that basal slip can occur quite easily due to the weak forces between adjacent layer planes means that the resolved shear stress necessary to produce basal slip would be small. Once initiated, slip would continue until all the basal planes are aligned nearly parallel to the stress direction, analogous to alignment of small permanent magnets in a magnet field along the magnetic

lines of force from an initial mosaic arrangement. This is accompanied by elimination of low-angle grain boundaries (Fig. 4), crystallite growth and increase in degree of graphitization (Table 1) and by an increase in preferred orientation (Fig. 6).

Above 20% deformation, the change in preferred orientation is small. This suggests that a different deformation mechanism is operative in this range. Several mechanisms which could account for this large deformation are: non-basal plane slip, fracture across a group of basal planes accompanied by sliding of this group with respect to adjacent basal planes, and slip along the basal planes which are at some small misorientation angle with respect to the stress direction without appreciable change in preferred orientation. Non-basal plane slip in graphite has never been identified or reported. The decrease in density of pyrolytic graphite which accompanies increasing deformation (Ref. 6) gives support to the postulated mechanism of fracture across a group of basal planes accompanied by sliding between adjacent groups of basal planes. Slip along basal planes at small misorientation angles without appreciable change in preferred orientation may also occur, but the data available are too limited to identify the extent of such deformation. It is possible that there are other mechanisms which could also contribute to the large deformations which have been measured.

This model considers basal plane slip as being the primary mode of deformation. While it accounts for the deformation which occurs when pyrolytic graphite is stressed parallel to the substrate, it does not explain how neighboring crystallites are joined nor does it explain why crystallite growth after heating to 3000°C and after 39% deformation at 2760°C is apparently limited to several thousand angstroms. One possible explanation for these phenomena is that strong cross-linking (Ref. 20) occurs between neighboring crystallites in pyrolytic graphite which impedes graphitization upon heating alone and upon heating and straining. Continuing work in this and other laboratories should aid in understanding graphitization in pyrolytic graphite and how neighboring crystallites are joined together.

IV. CONCLUSIONS

The results of this investigation may be summarized as follows:

1. The deformation of pyrolytic graphite which occurs when stress is applied parallel to the substrate direction at 2760°C involves several different mechanisms.
2. Deformations up to 20% are by basal plane slip and by basal plane orientation. This is accompanied by elimination of low-angle grain boundaries (dewrinkling), increase in preferred orientation, crystallite growth, and an increase in the degree of graphitization.
3. Deformations above 20% may be due to fracture across a group of basal planes accompanied by sliding between adjacent groups of basal planes and slip along basal planes at small misorientation angles without appreciable change in preferred orientation.
4. Heating to 3000°C. with no applied stress causes greater crystallite growth and a higher degree of graphitization than deforming 39% at 2760°C but the increase in preferred orientation is greater after deforming under load than after heating alone.

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